Chapter 3 - ATMOSPHERIC TRANSPORT AND MERCURY DEPOSITION

A. Introduction

Mercury is an especially dynamic pollutant because of its unique physical, chemical, and bioaccumulative properties. The volatility of the liquid elemental metal and some of its compounds, in conjunction with its ability to chemically transform under environmental conditions, makes it easily exchangeable across all environmental media including the biosphere where it can bioaccumulate and biomagnify. After release to the environment, mercury enters into what is referred to as the biogeochemical cycle, where it remains chemically, biologically, and environmentally dynamic for a sustained period of time, until it is ultimately sequestered in stable long-term environmental sinks such as the depths of the ocean, deep freshwater lake sediments, and soil (Fitzgerald et al. 1991). Retiring mercury from commerce, by sequestering it in a secure, permanent storage facility is intended to diminish input to the environment.

This section briefly outlines the many components of mercury fate and transport that influence the patterns of accumulation of mercury in the environment and subsequent exposure. These components are described more thoroughly in the first Mercury Task Force Report (NJDEPE 1993). Direct discharges of mercury to land and water will result in increased mercury in the environment, however this section will focus mainly on the fate and transport of emissions to air.

In the past, direct discharges of mercury to land and water were significant in NJ. One such historic example is the Ventron/Velsicol site which discharged as much as two to four pounds of mercury per day into Berry's Creek (see Chapter 7 of this Volume) up until 1974. These sources are much better regulated today, and it is believed that they now represent a very small portion of the new mercury added to the NJ environment each year. Work is still necessary to prevent mercury that is present on land from reaching water bodies in the state.

B. Emissions

The fate of mercury in the environment begins with emissions to air, land or water. Direct emissions to the air in NJ that result from human activities (anthropogenic emissions) have been studied in detail by this Task Force and are discussed in Volume III, of this report. These emissions come from a wide variety of sources including many types of combustion and the processing of mercury-containing wastes. Mercury from emissions elsewhere also contribute to mercury levels in NJ's atmosphere, and estimating the relative contribution of in-state to out-of-state sources is a challenge.

Globally, natural emissions to air are also a significant source category, contributing as much as 2.5 million kilograms per year (Nriagu 1989). Such emissions result from volcanoes, erosion, seasalt spray, forest fires, and particulate and gaseous organic matter emissions from land and marine plants. Nriagu (1989) estimates that natural sources make up about 41% of the total air emissions in the world, with about 40% of natural emissions coming from volcanoes and 30% emitted by marine plants. Other estimates place natural emissions closer to 20%. The contribution of natural sources in NJ is not known but is likely to be small since 1) the state does not have volcanoes within its boundaries, and 2) most of the coastal zone, where seasalt spray may make a contribution, is on the east or downwind coast.

It has been estimated that anthropogenic activities have increased global atmospheric mercury emissions by at least a factor of 3 relative to natural emissions since the beginning of the Industrial Revolution (Andren and Nriagu 1979).

C. Movement Through Air and Between Air and Land

As mercury is emitted to the atmosphere, it is moved and diluted by local winds. Some may be deposited locally, especially during precipitation events. Eventually the remaining mercury plume merges with the general air mass and becomes part of the global atmospheric pool of mercury. This circulates with prevailing air currents, continually receiving newly emitted mercury and losing it through wet and dry deposition on water surfaces or land. Some mercury that falls on land can run off, through rainfall and erosion, into a local water body. Mercury that reaches water bodies either directly or indirectly can be converted by biota into the more toxic methylmercury, which then biomagnifies up the food chain, where it accumulates reaching high concentrations in some of the longer-lived fish (see Figure 2.2).

D. Atmospheric Chemistry & Residence Times

The form in which mercury is emitted and the occurrence of rain and snow influence whether air emissions will be deposited close to a source or will be transported long distances before being deposited on land or water. If a water-soluble form of mercury (such as mercuric chloride) is emitted, it may be deposited close to the emission source during a precipitation event. If not deposited locally, much of this water-soluble mercury is likely to be washed out of the air within a day or two (as soon as a precipitation event is encountered). Non-soluble forms of mercury (such as elemental mercury) will travel much farther. These forms enter the global reservoir where they are slowly converted to soluble forms of mercury, mainly Hg^{++}, and then washed out. The residence time of non-soluble mercury in the atmosphere is about one year (Mason et al. 1994).

E. Deposition

Two types of mercury deposition occur: wet and dry. Wet deposition (via rain and other types of precipitation) is most efficient at removing divalent mercury (a soluble form) from the air. Dry deposition, via settling and scavenging, is more likely to remove particulate forms of mercury from the ambient air and can also remove gaseous mercury forms.

Whether the deposition is to land or water will define the possible pathways to bioaccumulation. The rate of bioaccumulation is dependent on many characteristics of the receiving water body. For example, the bioaccumulation rate in fresh water lakes will be different from the rate in a moving stream, which in turn is different from bioaccumulation in estuarine or marine waters.

1. Estimates of Wet and Dry Deposition of Mercury

Wet deposition of mercury can be measured directly by placing buckets to collect precipitation on a daily, weekly, or event basis. The water that is collected is then analyzed for total mercury, or occasionally even for specific forms of mercury. Reliable techniques for measuring dry deposition of mercury are not available, so indirect means of extrapolating dry deposition from observations of gaseous and particulate mercury in the air must be used. Algorithms have been developed to calculate the amount of mercury in the air that will deposit on the ground and on vegetation in the absence of rainfall.

When estimates of mercury deposition are needed over a large area, models are sometimes used to generate predicted deposition patterns. Some models are used to predict deposition from a single source or small group of sources within one to 50 kilometers of the point of emission. Other models have been developed to predict the transport and deposition of emissions from many sources over large areas. One such large-scale model (RELMAP) was used by USEPA to describe the impact of emissions throughout the country on wet and dry deposition nationwide (USEPA 1997a).

Models such as RELMAP (Regional Lagrangian Model of Air Pollution) and TEAM (Trace Elements Analysis Model), use a series of mathematical equations to represent the movement of mercury through the atmosphere and from the air to land and water. These models use meteorological data collected at hundreds of airports around the country to describe the dispersion of mercury. They also include a series of equations to describe the chemical reactions that convert mercury from one form to another. Assumptions regarding deposition velocity and scavenging rates (i.e., how fast precipitation can remove mercury from the air) are employed to estimate dry and wet deposition, respectively.

2. *Estimates of Total Deposition in NJ*

At present there are no definitive data that can quantify total wet and dry deposition of mercury in NJ. However, there are modeling and monitoring studies that provide insight into what the deposition is likely to be. These studies include: 1) the Northeast Mercury Study; 2) the Trace Elements Analysis Model; and 3) the NJ Atmospheric Deposition Network. Each of these is described briefly below and the deposition estimates are summarized.

a. *Northeast Mercury Study*

The Northeast Mercury Study (NESCAUM et al. 1998) includes a modeling analysis of mercury emission sources throughout the country. Using RELMAP, the dispersion of emissions from these sources was predicted for a one-year period using hourly meteorological data from 1989 (e.g. precipitation rates, wind speed and direction). From the predicted concentrations, both wet and dry deposition were estimated at grid squares representing about 1600 square kilometers each (roughly 25 mi x 25 mi).

The model used in this study predicted the total wet and dry deposition rates to be 30 to 100 $\mu g/m^2/yr$ over most of the state of NJ (with a few areas along the coast having predicted rates in the 10 to 30 $\mu g/m^2/yr$ range). When these results are integrated over the whole state (as described below in the discussion of relative contributions), the total deposition is estimated to be 610 to 1740 kg/yr. The Northeast Mercury Study estimates that the relative contribution of wet and dry deposition through the whole Northeastern region (New England, New York and NJ) is about 54% wet and 46% dry.

b. *Trace Elements Analysis Model*

The model TEAM (Pai et al. 1997) also predicts wet and dry deposition on a national scale. This model uses sophisticated atmospheric chemistry and wet and dry deposition algorithms. The model results (predicted for 10,000 square kilometer grid cells) reported by Pai et al. (1997) are based on 1990 emissions and meteorological data. The model predicts a range of wet and dry deposition rates for NJ, which are summarized below by region. The predicted range for total deposition is 24 to 80 $\mu g/m^2/yr$ (Table 2.2), which is similar to the range of deposition predicted in the Northeast Mercury Study.

Table 2.2. Predictions of Mercury Deposition in NJ from the TEAM Model.

NJ Region	Wet Deposition Rate ($\mu g/m^2/yr$)	Dry Deposition Rate ($\mu g/m^2/yr$)	Total Deposition Rate ($\mu g/m^2/yr$)
North	30-55	26-50	56-80
Central	15-20	8-17	24-32
South	20-30	8-12	24-32

c. NJ Atmospheric Deposition Network

The NJ Atmospheric Deposition Network (NJADN), sponsored in part by NJDEP, is collecting wet deposition and ambient concentration data for a whole suite of pollutants, including mercury, at nine sites around the state. The first site began operating in July 1998. The annual mean wet deposition of mercury, for the four sites in the network measuring wet depostion, is 15 $\mu g/m^2/yr$ (Eisenreich & Reinfelder 2001). This is higher than the value recorded at most of the sites in the National Atmospheric Deposition Program, which reported wet deposition of mercury with a median value of 9 $\mu g/m^2/yr$ and a range across 33 sites of 3.9 to 17.7 $\mu g/m^2/yr$ in 1999 (NADP, 2000). It is also well above the mean wet deposition in the United States and eastern Canada of 10 $\mu g/m^2/yr$ reported by Sweet et al. (1999), but lower than the wet deposition rates predicted by the two models described above. The difference between observed and predicted deposition is most likely due to a combination of two factors: a) conservative assumptions in the models that tend to result in overpredictions of deposition; and b) decreases in emissions from the timeframes used in the models (1990 for TEAM and 1997 for the Northeast Mercury Study) to the present time which is represented by the recent monitored data. Dry deposition estimates based on gaseous and particulate concentrations of mercury measured in the air are still under review. The mercury results of the NJADN are described in more detail in Chapter 7 of this Volume.

3. Relative Contributions of In-State and Out-of-State Emissions to Deposition in NJ

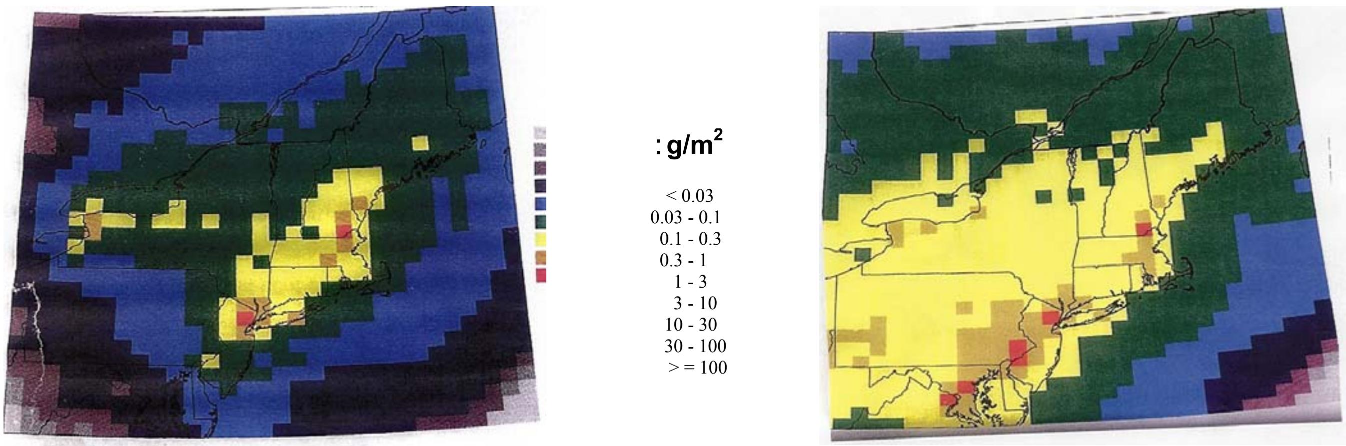
The Northeast Mercury Study (NESCAUM et al. 1998) provides some rough estimates of the relative contribution of in-state mercury emissions and out-of-state mercury emissions to total mercury deposition in NJ. The study reports the results of three model runs which included: 1) only sources located in the eight northeast states; 2) all other sources in the Unites States; and 3) only the global reservoir of mercury which is present throughout the world. These results are presented in a series of maps which show a range of wet and dry deposition for each grid cell in the region. (A grid cell is about 1600 square kilometers. The total area of NJ is about 21,700 square kilometers.) These results are summarized in Table 2.3.

The deposition estimates for the sources located in the eight Northeast States can be taken as a good representation of deposition in the state from NJ sources alone since this state is generally at the upwind edge of the region. Some of the deposition in the Northeastern grid cells may be influenced by emissions from sources in New York state; however, the impact of other northeast state sources in NJ should be rather slight in this model run. These model predictions (as presented in Figure 2.3, from NESCAUM et al. 1998) can be used to get a rough estimate of total deposition by summing across grid cells the product of the deposition rate ($\mu g/m^2/yr$) and the grid area (km^2). This calculation results in the values in the last column of Table 2.3. This estimated total deposition integrated over the whole state is about

610 to 1740 kg/year. This calculation indicates that the in-state sources could contribute about one-third of the total mercury deposition in the state.

Figure 2.3. Estimated Total Mercury Deposition in the Northeast from In-Region Sources and from All U.S. Sources.

Hg deposition from in-region sources | **Hg deposition from all U.S. sources**



Source: NESCAUM et al. Northeast States and Eastern Canadian Premiers Mercury Study - A Framework for Action. February 1998)

Table 2.3. Deposition Results Reported in the Northeast Mercury Study (NESCAUM et al. 1998).

Source of Mercury Emissions	**Range of Wet & Dry Deposition Rates in NJ**	**Estimated Total Deposition Integrated over NJ**
Sources Located in the 8 Northeast States	South: 3-10 $\mu g/m^2$ Northwest: 10-30 $\mu g/m^2$ Camden: 10-30 $\mu g/m^2$ Northeast: 30-100 $\mu g/m^2$*	200 – 650 kg/yr
US Sources Located Outside the 8 Northeast States	Southwest: 30-100+ $\mu g/m^2$ All other grids: 10-30 $\mu g/m^2$	340 – 870 kg/yr
Global Reservoir	Entire State: 3-10 $\mu g/m^2$	70 – 220 kg/yr
All Sources Combined	Some Coastal Grids: 10-30 $\mu g/m^2$ NE and SW Metro Areas: >100 $\mu g/m^2$ All other Grids: 30-100 $\mu g/m^2$	610 – 1740 kg/yr

* One grid cell shows deposition greater than 100 $\mu g/m^2$. This estimate was most likely influenced by two NJ sources which were modeled but are no longer in existence, so this result is not included in the table. Instead, it is assumed that the maximum deposition in this grid cell was 100 $\mu g/m^2$.

4. Uncertainty in deposition estimates

Many uncertainties make it difficult to assess the wet and dry deposition of mercury, either through monitoring of actual values or modeling of the transport and fate of mercury emissions to the ambient air. However, it is important to note that despite all of this uncertainty, comparisons between modeling and monitoring in many studies (including Pai et al. 1997 and NESCAUM et al. 1998) show a strong correlation between predicted and observed wet deposition rates.

Methods for measuring wet deposition of mercury are limited in their ability to characterize the spatial and temporal distribution of deposition by the investment and maintenance of sampling stations and the cost of analysis. Estimates of dry deposition are even more uncertain because they are extrapolated from air concentrations using various assumptions regarding deposition velocity for the various forms of mercury.

Models of mercury transport begin with a mercury emissions inventory which identifies, estimates and catalogues the mercury emitted from various source types. The quantity of mercury emissions, the location of the emissions, and the chemical form of the mercury when it is emitted are all sources of uncertainty. Although substantial progress has been made in identifying the quantity and location of mercury emissions, there is still a great deal of work to be done in identifying the chemical form. Knowledge of the speciation is especially critical when predicting wet and dry deposition rates since they vary from one species to another. Mercuric chloride, for example, is much more water soluble than elemental mercury and, therefore, is more likely to be absorbed by rainwater and to be deposited close to its source.

Seigneur et al. (1999) have carried out an extensive analysis of the uncertainties associated with model predictions of human exposure to mercury through the consumption of fish. This analysis considered three prediction tools that must be used together to make such estimates of mercury ingestion. These tools are: a) the atmospheric transport and fate model; b) the watershed and biota bioaccumulation model; and c) the model of fish consumption patterns. The atmospheric transport and fate model variables included in their uncertainty analysis were mercury emission speciation, ozone atmospheric concentration, atmospheric precipitation, mercury atmospheric background concentration, mercury deposition velocity, and cloud water pH. Of these variables, mercury emission speciation contributed the most to the model uncertainty.

5. Summary: Transport and Deposition

Some mercury, particularly mercury that is emitted as soluble mercury or as particulates, deposits locally. The remaining mercury eventually enters the global atmospheric pool of mercury. The residence time of non-soluble mercury in the atmospheric is about one year. Eventually atmospheric mercury deposits on surfaces from which it can be transported directly to water bodies.

Total deposition rates for mercury in NJ have been predicted in the Northeast Mercury Study to be on the order of 10 to 100 $\mu g/m^2/yr$ and in the TEAM Study to be about 24 to 80 $\mu g/m^2/yr$. These two studies give comparable total deposition rates. The wet deposition rates observed by the NJADN are on the order of 15 $\mu g/m^2/yr$. This is on the lower end of the wet deposition range predicted by TEAM (15 to 55 $\mu g/m^2/yr$). The Northeast Mercury Study does not break out wet deposition for NJ alone, but it does estimate the relative contribution of wet to dry deposition for the region to be about 46% dry and 54% wet. Using this ratio would give a NJ wet deposition rate of 5 to 54 $\mu g/m^2/yr$, which is about the same range as TEAM and includes the NJADN rate within its bounds. It has been estimated that the NJ emissions account for about one-third of the mercury which deposits in NJ.

F. Recommendations

Maintain and enhance a long-term air deposition monitoring system that incorporates state-of-the-art detection limits and speciation to document temporal and spatial trends in mercury deposition (Recommendation "L" in Volume 1).

Information regarding deposition of mercury in NJ is still quite limited. Both modeling and monitoring approaches should be pursued to fill this gap. The information gathered in this way can be used to assess the current status of deposition in the state and to follow trends as emission reduction programs are put into place. These tools might also be used to provide a rough estimate of the portion of deposition attributable to in-state sources and to out-of-state sources. Recommendations regarding the development of these tools follow.

Air Monitoring: Long-term air deposition monitoring sites should be established in NJ. Some of the sites may be the same as those currently in the NJ Air Deposition Network that is operated by Rutgers and funded, in part, by NJDEP. Site locations should be selected so that deposition of mercury emitted out-of-state can be distinguished from mercury emitted in the state. Sampling frequency for particulate mercury may be every 12^{th} day at some of the sites, but a subset should be enhanced to collect particulate mercury data every 6^{th} day. Weekly samples of wet deposition should be collected.

Deposition: The Department should have access to a state-level version of the EPA model for fate and transport (RELMAP) that can be run using the up-to-date emissions inventory that has been developed by the Mercury Task Force. The results of this modeling effort, combined with new EPA model results for the whole country, thus will provide a better estimate of the relative contribution of in-state and out-of-state sources and can be used in subsequent years to predict the local benefit of reduction strategies.

Since the air emissions of mercury in NJ do not appear to account for the majority of the mercury deposition in the state, it is very important that the NJDEP continue to press for national mercury emission reduction programs.